

Suppression of High Speed Flames and Quasi-detonations

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ABSTRACT

Past research has identified three candidates as near term replacements for CF_3Br in some aircraft total-flooding fire protection applications: CF_3I , C_2HF_5 and C_3F_8 . The behavior of these compounds when added to lean, stoichiometric and rich propane/air mixtures exposed to subsonic and supersonic combustion waves is examined using a 10 m long, 50 mm diameter detonation/deflagration tube. Pressure and visible radiation are measured as a function of the amount of agent in the mixture to determine the pressure ratio across the incident shock wave and the speed of the radiation front. The results are compared to earlier studies using ethene, in which significantly higher pressure ratios and wave speeds were generated. The presence of the three extinguishing compounds in the propane/air mixtures causes the combustion either to be enhanced or suppressed, and depending upon the dynamical situation and the concentration of the agent, any of the three can outperform the others. For example, C_3F_8 is the most effective compound for attenuating combustion systems for all stoichiometries; C_2HF_5 reduces the threat by 90 % when its volume fraction is 11 %, the best performance of the three, but amplifies the severity of the deflagration the most at a volume fraction of 5 %; and the best agent for attenuating the pressure increase of the shock wave is CF_3I under most conditions.

KEYWORDS: fire suppression, detonation tube, aircraft fires, halon alternatives

INTRODUCTION

The elimination of new production of CF_3Br (halon 1301) has forced users of total flooding-type fire protection systems to seek alternatives. Most research has concentrated on finding substitutes for fighting fires involving fuels which are solid or flammable liquids and with growth times that

are from seconds to minutes, necessitating agent release times of a few seconds and longer. For these applications small pool fires, diffusion flames and low speed deflagrations are useful laboratory tools for evaluating the effectiveness of the agents, and for unraveling their modes of operation.

Halon 1301 is also used on very rapidly growing fires and to mitigate the danger of explosions which could threaten, for example, manufacturing operations or transportation systems. High speed deflagrations and detonations are a particular concern for the military in both combat and noncombat operations. In these situations, the fuel may be in the vapor state and premixed with air. Ignition may be followed by a rapidly accelerating turbulent flame, which, under the right set of conditions, may make a transition to a detonation. Combustion time scales are on the order of milliseconds, requiring that the agent be released rapidly (less than 100 ms) if intervention is to be effective. The performance of an agent in suppressing a pool fire or low speed deflagration may not be a good predictor of its behavior in a high speed turbulent flame or a detonation since the time scales and pressures are not replicated properly.

Rapid pressure increases and high speed combustion waves can be produced in a detonation/deflagration tube, making it a suitable device for studying in a controlled manner the impact of various agents on the combustion intensity. Gmurczyk and Grosshandler [1] used a 7.5 m long, 50 mm diameter detonation/deflagration tube to compare the behavior of shock waves and quasi-detonations in lean and stoichiometric ethene/air mixtures inhibited with CF_4 , CHF_3 , CHF_2Cl , CF_3Br and CF_3I . The heart of their apparatus is shown schematically in Fig. 1. On the left side of the figure is a portion of the driver section. Just prior to ignition (with a spark), the gate valve was opened. The combustion/shock wave was fully established before entering the test section. The driver section was filled with a combustible mixture of fuel and air; the test section contained the gaseous agent along with the same fuel/air mixture used in the driver section. They found the system highly reproducible and capable of clearly discriminating among the various extinguishing compounds. CF_4 was identified as the most effective in decreasing the final pressure, wave speed, and visible radiation. CHF_2Cl was the least effective, with mole fractions between 2% and 10% causing the shock pressure wave and speed to be enhanced.

Perfluoro- and hydrofluoro-carbon compounds containing two, three, and four carbon atoms were examined in the same facility by Gmurczyk et al.[2] The superior performance of the perfluoro compounds under lean conditions identified in the parallel study above was shown to hold for the higher molecular weight compounds as well. They also found that a 6 % mole fraction of C_2HF_5 added to a lean C_2H_4 /air mixture about doubled the pressure build-up across the shock wave compared to the uninhibited conditions.

In the prior studies the ethene/air mixtures were lean and stoichiometric, which produced quasi-detonations with pressure ratios greater than 18:1 and wave speeds as high as 1400 m/s. The intent was to challenge the agents under very severe conditions. Pressure ratios previously observed in full-scale testing of uninhibited propane air mixtures have been reported to be less than 7:1, and photographic evidence from the Wright Patterson AFB test program with jet fuels suggests that turbulent flames (rather than quasi-detonations) with speeds below 300 m/s are common. The current paper investigates the behavior of CF_3I , C_3F_8 and C_2HF_5 under conditions which are closer to these field observations, but still severe enough to answer questions regarding their possible application to other explosion protection situations. The agents were chosen because they also

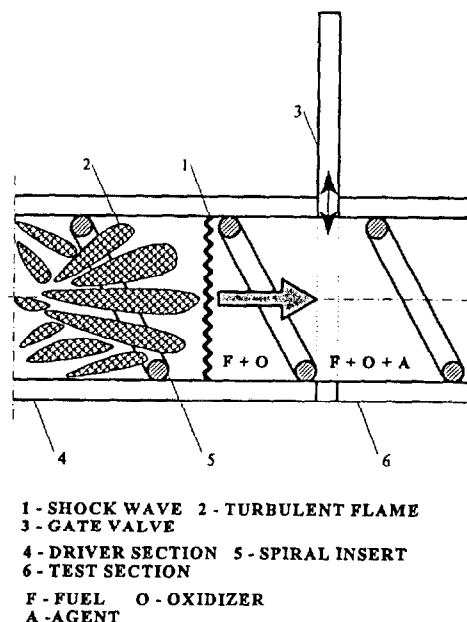


FIGURE 1. Schematic of combustion wave entering test section

were to be included in the full-scale aircraft mock-up fire testing conducted at Wright Patterson AFB [3].

EXPERIMENTAL FACILITY

The same facility described by Gmurczyk and Grosshandler [1] was used in the current study. The spiral insert intentionally added to the test section to generate turbulence and accelerate the flame was removed to reduce the combustion intensity. The test section was doubled in length to 5 m to allow determination of the slower combustion wave speeds without interference from reflected shocks. Propane replaced ethene because it is less reactive. All of these changes acted to reduce the pressure ratios and propagation speeds of the uninhibited combustion waves.

The incident shock wave speed and pressure ratio were determined from piezoelectric transducer signals, and the time between activation of photodiodes was used to calculate the speed of the visible radiation front. Transducers were located 2.2 m beyond the gate valve in the original 2.5 m long test section. The photo diodes in the 5.0 m long test section are located close to the entrance region, 0.3 m downstream of the gate valve, to better ascertain the immediate impact of the inhibitor on the flame dynamics; the shock signals are measured 2.2 m into the test section, which is the same location used with the short tube.

Gas mixtures were established from the partial pressures of the fuel, air, and agent components

measured with static pressure transducers. The absolute uncertainty in partial pressure percentages reported is estimated to be less than $\pm 0.3\%$. The initial temperature and total pressure were maintained constant at $22\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ and $100\text{ kPa} \pm 0.6\text{ kPa}$, respectively. The accuracy of the shock wave measurements is affected by the dynamic pressure transducer, amplifiers, data acquisition system, and readout device. Assuming additivity of errors, the resultant accuracy of determining the shock pressure is $\pm 2.2\%$. The shock speed is estimated to be accurate to better than $\pm 4.4\%$ of the reported value, while the combined accuracy of the radiation wave speed is estimated to be $\pm 2\%$ of the range. Additional details of the facility design, measuring equipment, data acquisition and operating procedure are provided in the NIST special publications describing the overall program [3,4].

EXPERIMENTAL RESULTS

The following independent parameters were changed during the course of the experimental project: type of suppressant (C_2HF_6 , C_3F_8 , and CF_3I); partial pressure of suppressant; type of fuel (ethene or propane); equivalence ratio of the combustible mixture (lean, stoichiometric, rich); geometry of the tube (2.5 m or 5 m long test section, with or without spiral). The dependent parameters that characterize the combustion within the test section are the pressure rise across the shock, the speed of the shock, and the speed of the radiation front.

The precision of the measurements was checked by replicating one test condition eleven times. The maximum relative deviations of the dependent parameters were found to be $\pm 10\%$ for radiation wave speed, $\pm 5\%$ for the shock speed, and $\pm 5\%$ for the shock pressure ratio.

Characterization of Combustion in the Detonation/deflagration Tube

The effect of the stoichiometry on uninhibited ethene/air and propane/air pressures and wave speeds was evaluated in the 2.5 m test section, with and without the spiral insert in place. Figure 2 compares the pressure ratios in the two fuel mixtures. The shock wave generated by the accelerating flame is detectable for equivalence ratios between 0.50 and 2.1 for ethene, and between 0.65 and 1.45 for propane. The peak pressure ratio is 35 to 1, which occurs when the ethene/air equivalence ratio is 1.25 and the spiral obstacle is in place. A stoichiometric mixture of propane produces a maximum pressure ratio of 26:1. Removing the spiral insert from the test section greatly decreases the shock pressure ratios for both fuel mixtures except for ethene/air equivalence ratios near 1.5.

The combustion wave speeds are shown in Fig. 3. The photo diode signals yield wave speeds identical to the pressure transducer signals when speeds are in excess of 800 m/s, indicating that the radiation wave travels in tandem with the shock wave in the quasi-detonation regime. A maximum shock speed of about 1300 m/s was recorded for stoichiometric propane with the spiral in place, less than the 1550 m/s speed found in the ethene/air mixture at slightly richer conditions. Removing the spiral insert significantly reduces wave speed in lean and rich propane mixtures, in contrast to ethene mixtures, in which detonation speeds over 1800 m/s were recorded for equivalence ratios between 1.25 and 1.75 with the spiral absent.

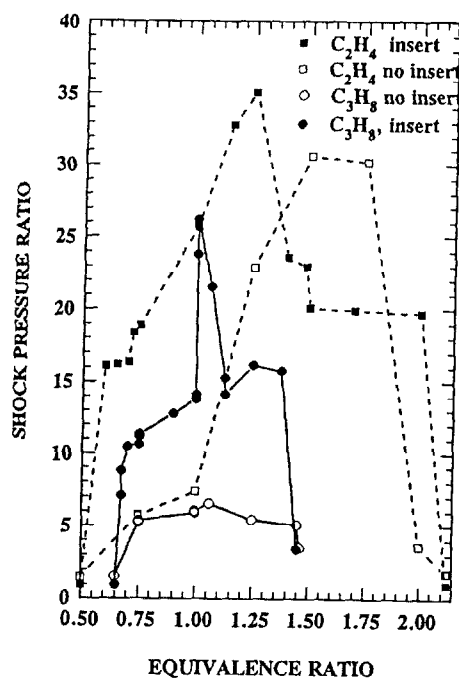


FIGURE 2. Shock pressure ratios vs. equivalence ratio comparing ethene and propane mixture (2.5 m test section).

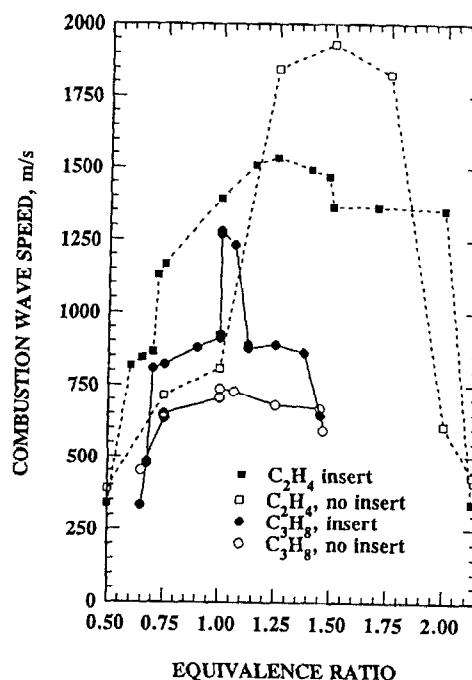


FIGURE 3. Combustion wave speeds vs. equivalence ratio comparing ethene and propane mixtures (2.5 m test section).

Four combustion modes can be identified with the ethene/air experiments: low-speed deflagration, high-speed deflagration, quasi-detonation, and Chapman-Jouguet condition. The latter condition does not occur with propane in the current facility. When the spiral is not present in the test section, the quasi-detonation regime of propane combustion also disappears. While the detonation process is unable to develop in the propane/air mixture when the spiral insert is missing from the tube, it is noteworthy that for the first time a quasi-detonation in a propane/air mixture has been recorded in the presence of the spiral obstacle. This finding extends the results of Lee [5] and Peraldi et al.[6]

A series of experiments was run with pure nitrogen in the test section to establish baseline pressure ratios and wave speeds for conditions known to be totally nonreactive. These are summarized in Table 1 for lean, stoichiometric and rich mixtures of ethene and of propane, for the 2.5 m and 5.0 m long test sections. The highest residual pressure wave ($P_1/P_0 = 5.0$) and shock speed (730 m/s) were found in the 5.0 m long test section with no obstacles present, generated by a rich ethene/air mixture in the driver section. For the two tests run with the spiral insert in the flow, the shock pressures and speeds were noticeably attenuated due to viscous dissipation across the obstacles. The nitrogen quenched all visible radiation in the short test section with the insert. The radiation intensity was sufficient in the experiments run with the 5.0 m long test section to measure wave speeds well below sonic conditions. This apparent difference in behavior of the short and long test

TABLE 1. Pressure ratio, shock speed and combustion wave speed comparing fully suppressed (100% N₂) to totally unsuppressed (0% N₂) test conditions.

Fuel Mix- ture	Test Sec- tion	0% Nitrogen			100% Nitrogen		
		P ₁ /P ₀	V _{shock} (m/s)	V _{comb} (m/s)	P ₁ /P ₀	V _{shock} (m/s)	V _{comb} (m/s)
C ₂ H ₄ , Φ=0.75	2.5 m (spiral)	18	1170	1170	2.5	440	0
	5.0 m (no spiral)	6.2	710	600	4.1	600	0
C ₂ H ₄ , Φ=1.00	2.5 m (spiral)	26	1400	1400	3.5	450	0
	5.0 m (no spiral)	6.5	720	720	4.7	660	0
C ₂ H ₄ , Φ=1.25	2.5 m (spiral)	35	1530	1530	*	*	*
	5.0 m (no spiral)	11	940	930	5.0	730	20
C ₃ H ₈ , Φ=0.86	2.5 m (spiral)	11	815	815	*	*	*
	5.0 m (no spiral)	8.1	690	330	4.5	575	103
C ₃ H ₈ , Φ=1.00	2.5 m (spiral)	13.5	900	900	*	*	*
	5.0 m (no spiral)	8.8	695	620	4.7	619	105
C ₃ H ₈ , Φ=1.25	2.5 m (spiral)	16	890	890	*	*	*
	5.0 m (no spiral)	8.3	690	510	4.5	586	45

* no data available

sections can easily be explained by the difference in measurement location. In the long test section the photodiodes were only 0.3 m behind the gate valve so that portions of the turbulent combustion emanating from the driver section were visible to the photodiodes either directly or through reflection. For comparison, the pressure ratios and wave speeds measured when the test section contained the same mixture as the driver section (ie., 0 % additional nitrogen in the fuel/air mixture) are also given in Table 1.

Suppression Performance of C_2HF_5 , C_3F_8 , and CF_3I

The relative performance of the three candidate agents is assessed by comparing the pressure ratios and velocities attained in the lean, stoichiometric, and rich propane/air mixtures in the 5.0 m long test section containing no spiral insert. Figure 4 is a plot of the pressure ratios measured across the shock wave at a location 2.2 m beyond the gate valve as a function of the agent partial pressure. The upper curves correspond to a fuel/air equivalence ratio of 0.86, the middle curves refer to stoichiometric combustion, and the lower group is fuel rich. For the lean condition, the initial pressure ratio is 8.1. It changes little with increasing partial pressures of C_2HF_5 or C_3F_8 . The CF_3I , on the other hand, reduces the pressure ratio even when its partial pressure is only 1%. The initial pressure ratio is a bit higher when the mixture is stoichiometric. The C_2HF_5 does not alter the pressure significantly even when it is present with a partial pressure of 10 %. The C_3F_8 slightly enhances the pressure build up at low partial pressures. The CF_3I drops the pressure ratio for the stoichiometric combustion in a manner similar to the lean combustion up to a partial pressure of 4 %, where a plateau is reached. The pressure ratio then remains about constant until a partial pressure of 15 % is attained, at which point the pressure wave is attenuated almost as much as if 100 % nitrogen had been added. The behavior of the pressure ratio under the rich condition is similar to that under the lean condition for the C_3F_8 and CF_3I . The C_2HF_5 works better to reduce pressure build-up under rich conditions, but is not as effective as CF_3I when present at the same partial pressure.

The radiation wave velocities measured under lean, stoichiometric and rich conditions for each of the agents are plotted in Figs. 5, 6 and 7. Starting from just about sonic conditions when no inhibitor is present, all three chemicals tend to enhance the combustion when added in small concentrations to the lean mixtures (Fig. 5). The C_2HF_5 drops the radiation wave speed to around 100 m/s when its partial pressure is 3 %, but then acts to accelerate the combustion wave to 500 m/s at a 6% partial pressure. The radiation is fully extinguished when the partial pressure is further increased to 8%. The CF_3I undergoes similar transitions from inhibitor to accelerant; however, the full extinguishing point is reached when the partial pressure is only 6 %. The C_3F_8 also extinguishes the reaction at 6 %.

In Fig. 6 (stoichiometric propane/air mixtures) C_3F_8 causes the combustion wave speed to decrease in a monotonic manner, with suppression occurring when the partial pressure fraction is 8 %. Full suppression is attained with C_2HF_5 at a concentration of 10 %; however, 2 % and 6 % levels of C_2HF_5 strongly enhance the exothermic reaction. The CF_3I is relatively well behaved, but requires the largest amount (on both a molar and mass basis) of the three agents to fully quench the radiation. Rich mixtures, shown in Fig. 7, require the least amount of C_2HF_5 and C_3F_8 to extinguish the flame radiation: 6 % and 4 % partial pressure, respectively. A partial pressure of 8% is needed for the same degree of suppression when the agent is CF_3I .

Performance Parameter

The exact conditions that are likely to exist prior to a fire or explosion are impossible to control. Unfortunately, the relative behavior of the three agents under investigation is strongly dependent upon the initial conditions, causing one chemical to be clearly superior under one arrangement and the same chemical to perform poorly in another. In an attempt to identify the best overall chemical

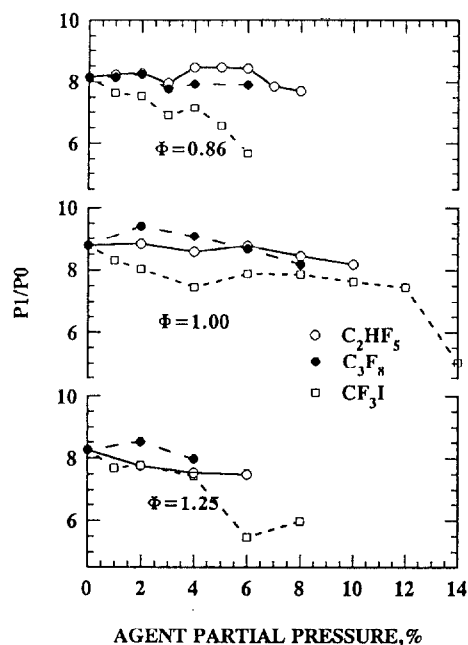


FIGURE 4. Shock pressure ratios vs. agent partial pressure in propane/air.

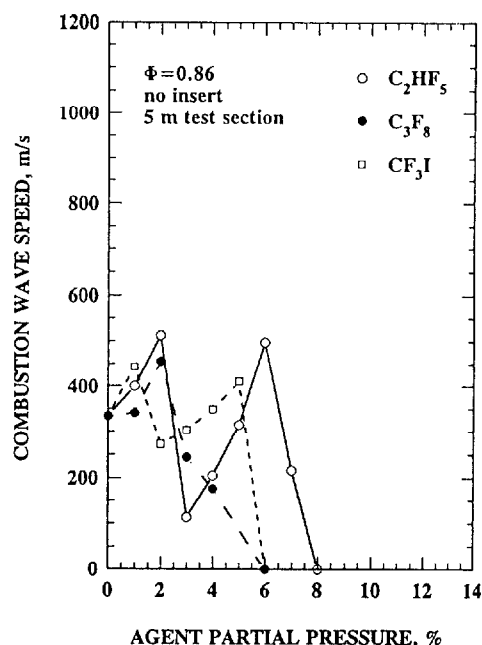


FIGURE 5. Radiation wave velocity vs. agent partial pressure in lean propane/air.

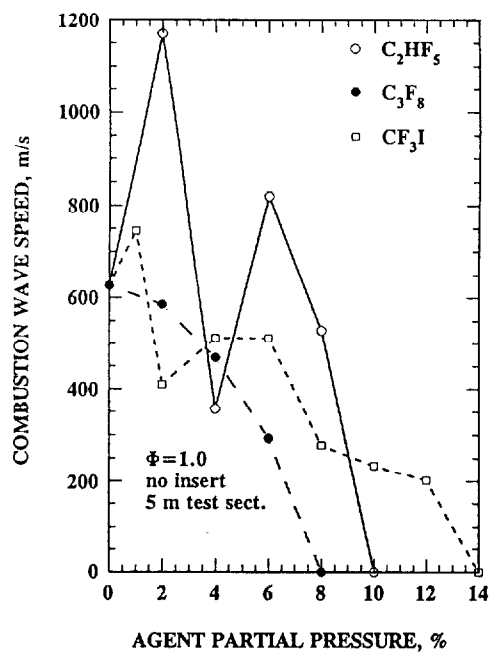


FIGURE 6. Radiation wave velocity vs. agent partial pressure in stoich. propane/air.

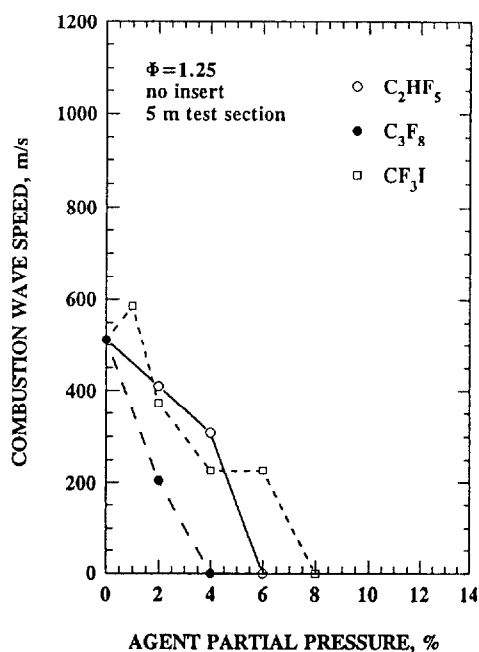


FIGURE 7. Radiation wave velocity vs. agent partial pressure in rich propane/air.

for an uncertain application, the response parameter, Ψ , is defined as

$$\Psi \equiv 1 - \frac{x - x^*}{x_0 - x^*}$$

where x_0 is the value of the parameter of interest (radiation wave speed, shock speed, or shock pressure ratio) when no agent is present and x^* is the corresponding value when extinction has occurred. A value of zero for Ψ means that the agent has no beneficial impact on the combustion process; $\Psi < 0$ implies the agent exacerbates the situation; a performance parameter near unity indicates close to total suppression.

The performance parameters are plotted in Figs. 8, 9 and 10 for C_2HF_5 , C_3F_8 and CF_3I , respectively. The volume percents plotted on the abscissa are identical to the partial pressure fractions for ideal gas mixtures. This is a reasonable approximation for the close-to-ideal mixtures under investigation in this work. The volume percent of agent is also a more conventional way to compare the performance of different compounds.

The open circles in the figures represent single measurements of radiation wave speed, shock speed or pressure ratio for the lean, stoichiometric or rich mixtures of ethene/air or propane/air, for the 2.5 m or 5.0 m test sections, and for the spiral insert removed or in place. In a number of cases, a single symbol corresponds to multiple overlapping measurements with identical values for Ψ . A value for Ψ much in excess of -1.0 in the negative direction was achieved on a number of occasions for each of the agents, most notably for C_2HF_5 , but also for CF_3I . The averages of Ψ are shown as the dotted lines in Figs. 8 through 10. The reason that the dotted lines do not look to represent the averages is that Ψ takes on multiple values of unity when the agent volume fractions are greater than about 10 %, and that the off-scale negative values weight Ψ in that direction when the agent is present in lower volume fractions. All data were included when computing the averages.

Comparing the three curves one gets an indication of general trends, and where one agent is likely to out-perform another. The C_3F_8 , on average, reduces the threat by 50% ($\Psi = 0.5$) when the volume fraction is 5 %, in contrast to about 8 % for C_2HF_5 , and just under 10 % for CF_3I . Based upon limited data gathered in [4] for CF_3Br/C_2H_4 /air mixtures, a volume fraction of about 3.7 % of halon produces a value of 0.5 for Ψ .

When the C_2HF_5 volume fraction is 5 %, Ψ is -0.85, indicating that, on average, the situation is much worse than had no agent been added. While the negative value of Ψ for an 8% volume fraction of CF_3I seems inconsistent with the agent's relatively positive performance demonstrated in Figs. 4 through 7, there was one instance where this amount of CF_3I added to a stoichiometric mixture of C_2H_4 /air caused a transition to a detonation [3, p. 54]. That test was repeated three times to assure that it was no fluke.

The volume percentages necessary to quench the radiation and reduce the pressure build up equivalent to 100 % nitrogen in the test section are summarized in Table 2 for the different fuel mixtures and tube geometries examined. From the composite results of the performance parameter plotted in Figs. 8 through 10, a 90% reduction in the threat requires 14% CF_3I , 13% C_3F_8 , and 11% C_2HF_5 . Total extinction of the exothermic reaction under all conditions examined in this study

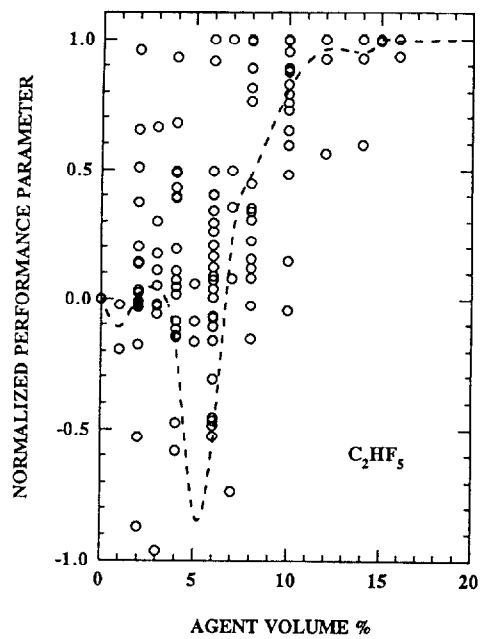


FIGURE 8. Performance of C_2HF_5 for all conditions in detonation/deflagration tube.

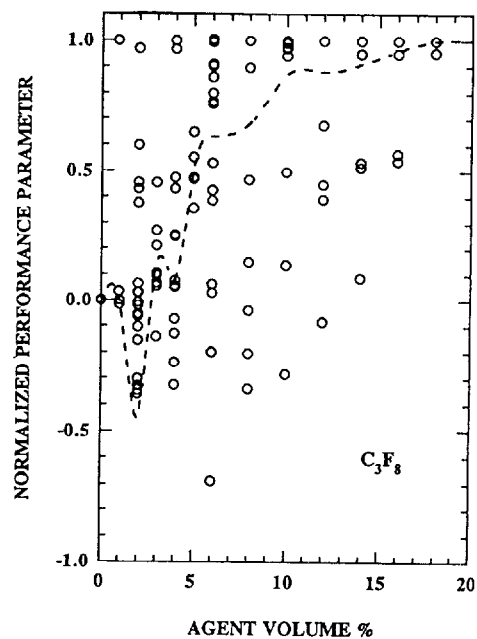


FIGURE 9. Performance of C_3F_8 for all conditions in detonation/deflagration tube.

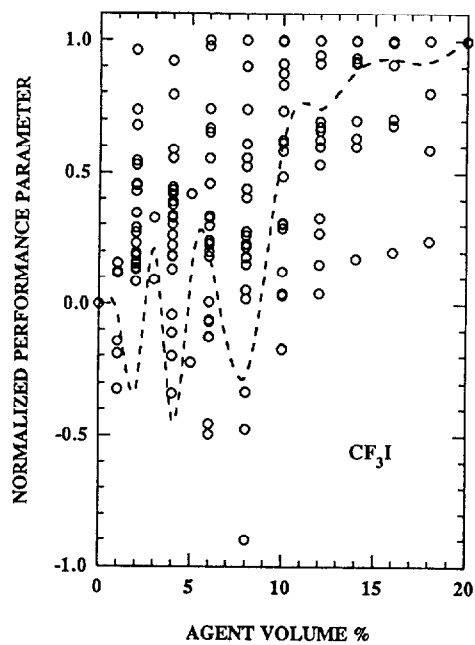


FIGURE 10. Performance of CF_3I for all conditions in detonation/deflagration tube.

TABLE 2. Suppression volume fractions in detonation/deflagration tube

Agent	Fuel and Equivalence Ratio					
	Ethene ^a $\Phi = 0.75$ Quasi- detonation	Ethene ^a $\Phi = 1$ Quasi- detonation	Ethene ^a $\Phi = 1.25$ Quasi- detonation	Propane ^b $\Phi = 0.86$ Turbulent Flame	Propane ^b $\Phi = 1.0$ Turbulent Flame	Propane ^b $\Phi = 1.25$ Turbulent Flame
C ₂ HF ₅	13 to 15 %	13 to 15 %	13 to 15 %	7.5 to 8 %	9 to 10 %	5 to 6 %
C ₃ F ₈	8 to 10 %	> 10 %	> 10 %	5 to 6 %	7 to 8 %	3 to 4 %
CF ₃ I	> 10 %	> 12 %	13 to 14 %	5.5 to 6 %	13 to 14 %	7 to 8 %
CF ₃ Br	7 to 10 %	c	c	c	c	c

^a 2.5 m test section, with spiral insert, measurement location 2.2 m into test section

^b 5.0 m test section, without spiral insert, measurement location 0.3 m into test section

^c no data

requires greater than 18%, 18% and 16%, respectively, of CF₃I, C₃F₈ and C₂HF₅.

It is instructive to compare the result shown in the table to those measured in other facilities. The most data available are for C₂HF₅. The volume fraction necessary to extinguish a small burning pool is about 8 % to 10 % in either a counter- or co-flow configuration, depending upon the fuel [4]. A baffle-stabilized fire of JP-8 with air flowing horizontally was extinguished when the volume fraction of C₂HF₅ was between 7.5 % and 20.9 %, depending on the exact conditions in the experiment [3]. A volume fraction of 12 % is the estimated flammability limit of C₂HF₅ premixed in a laminar, stoichiometric propane/air flame [3]. The phase II dry-bay tests performed at Wright-Patterson AFB were conducted in test articles almost 3 m³ in volume using JP-8 fuel, with the ignition source an anti-aircraft round. Based upon their data [7], the amount of C₂HF₅ required to extinguish this high speed turbulent flame is estimated to range from 14 % to 24 % by volume. The current results shown in Figure 8 indicate that lesser volume fractions of C₂HF₅ are necessary to quench the reaction in the detonation/deflagration tube.

The cup burner value for C₃F₈ with heptane is 6.3 % by volume [3]. The Air Force study [7] found that between 9 % and 25 % was required to control the full-scale, mock dry-bay fires, an amount which straddles the values plotted in Fig. 9 for C₃F₈. Using CF₃I as the agent, 3.2 % by volume is required to extinguish the heptane cup burner flame; the estimated minimum dry-bay volume fractions are from 2.6 % to 7.4 %. The CF₃I performs, on average, significantly poorer in the detonation/deflagration tube, where volume fractions well in excess of 10 % are needed to eliminate the threat posed by high-speed combustion waves and quasi-detonations (see Fig. 10).

CONCLUSION

Depending on their concentrations, the presence of the three extinguishing compounds in the propane/air mixtures causes the combustion either to be enhanced or suppressed, often with complex extrema exhibited. The erratic behavior is diminished when the mixtures become richer

in fuel content. C_3F_8 is the most effective extinguishing compound in suppressing and attenuating combustion waves in lean, stoichiometric, and rich ethene/air and propane/air mixtures. The high over-pressures observed previously when C_2HF_5 was added to ethene/air mixtures were not as prevalent during suppression of propane/air mixtures. CF_3I is the best agent for attenuating shock pressure ratio in the lean, stoichiometric and rich propane/air mixtures; however, compared to its superior performance in cup burner tests and in suppressing pool fires, a higher volume fraction of CF_3I is necessary to ensure total suppression in the detonation/deflagration tube than those required by C_3F_8 or C_2HF_5 .

The key conclusion of this study is that chemicals being considered as alternatives to halon 1301 perform differently, in both an absolute and relative sense, when evaluated under differing fire conditions. Careful and extensive testing is required under conditions which replicate the intended application to ensure that the hoped-for performance is actually attainable.

ACKNOWLEDGMENT

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